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# Boosting diethylamine selective oxidation over CuO/ZSM-5 catalyst by $CeO_2$ modification

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# ABSTRACT

Selective catalytic oxidation of nitrogen containing volatile organic compounds (NVOCs) is very meaningful but still remains big challenge because it is very difficult to balance the oxidation activity and N<sub>2</sub> selectivity of available catalysts. In order to develop excellent catalysts with high N2 selectivity in wide temperature window  $(\Delta T)$  during NVOCs oxidation, CeO<sub>2</sub> modified CuO/ZSM-5 catalysts with different CeO<sub>2</sub> addition order were prepared for diethylamine (DEA) oxidation. Detailed characterizations of catalysts such as XRD, XPS, H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD were conducted, it is found that addition of CeO<sub>2</sub> obviously changes the geometrical and electronic states of CuO active sites in the catalyst, and CeO<sub>2</sub> addition order affects the  $Ce^{3+}$  ratio on the catalyst surface. Promotion of CeO<sub>2</sub> species enables the generation of more highly active Cu species (Cu<sup>+</sup> species and finely dispersed CuO clusters) for DEA oxidation; and synergistic catalysis of the Ce<sup>3+</sup> species, active Cu species and acid sites in ZSM-5 leads to the high N<sub>2</sub> selectivity in wide temperature window ( $\Delta T$ ). Compared to the CeO<sub>2</sub>/ CuO/ZSM-5 and CuO-CeO2/ZSM-5 catalysts, the CuO/CeO2/ZSM-5 catalyst exhibits moderate high oxidation activity with  $T_{99}$  of 230 °C and the widest  $\Lambda T$  of 150 °C for high N<sub>2</sub> selectivity. Our primary results in this work provide the efficient strategy for improving catalyst employed for NVOCs selective oxidation.

#### 1. Introduction

Nitrogen containing volatile organic compounds (NVOCs), such as DMF, CH<sub>3</sub>CN and acrylonitrile, are hazardous for both humans and environment, and a large amount of NVOCs are still constantly emitted into exhaust gas up to date. [1-7] Selective catalytic oxidation of NVOCs has drawn more and more attentions because NVOCs could be transformed into harmless substance of H<sub>2</sub>O, CO<sub>2</sub> and N<sub>2</sub> by this technology. [8-13] However, there is also some challenges need to be addressed in the field of catalytic oxidation NVOCs. On one hand, it is preferred that the employed catalysts show excellent oxidation activity and could catalyze NVOCs complete oxidation at low temperature to save energy cost. On the other hand, high selectivity to CO2 and N2 in NVOCs oxidation is also demanded to prevent the production of secondary pollution of CO and NO<sub>x</sub> for environment. Enhancing the catalytic oxidation activity is commonly compromised by the deterioration in N<sub>2</sub> selectivity. Thus, balance of catalytic oxidation activity and N2 selectivity for NVOCs oxidation still remains big challenge up to date, which seriously limits the wide application of selective catalytic oxidation for NVOCs elimination.

To overcome such challenges, great efforts have been devoted to the development of catalysts with high oxidation activity and high N2 selectivity in a wide temperature window. Both noble metal (Pt, Pd) [14-15] and non-noble metal (Cu, Mn) [16-18] catalysts have been considered to be employed into NVOCs oxidation. Whereas, it was reported that non-noble metal based catalysts such as CuO, MnO should be more suitable for NVOCs selective catalytic oxidation because of their high N<sub>2</sub> selectivity. As for the CuO based catalysts, there are also many critical factors, including CuO chemical states, surface property of support and promoter effect, that affect their terminal performance for NVOCs selective catalytic oxidation. [19-22] Generally, highly dispersed CuO or isolated Cu<sup>2+</sup> species are regarded as the critical active sites for NVOCs selective oxidation, which not only affect the oxidation activity but also change N<sub>2</sub> selectivity of catalyst for NVOCs complete oxidation, thus many efforts have been devoted to modulate CuO states in the catalyst. [23-25] The sorts of zeolites had remarkable effect on the

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chemical states of CuO species, CuO dispersion of Cu-zeolites decreased in the following order: Cu-ZSM-5 > Cu-SAPO-34 > Cu-MOR > Cu-MCM- $22 > Cu-H\beta$ . [19] Besides, the Si/Al ratio in zeolites also has influence on the states of CuO species, more highly dispersed CuO would generate on the ZSM-5 with lower Si/Al ratio. [20] Preparation condition of catalyst such as calcining temperature also affect the states of CuO species, Leng et al. found the optimal calcining temperature of CuO supported on SSZ-13 at 450 °C. [21] Addition promoter of CeO<sub>2</sub> would also change the states of CuO due to the good redox and oxygen storage properties of CeO2. Therefore, CeO2 modified CuO based catalyst (such as CuO/ZSM-5, CuO/UZM-9) by co-impregnation method have been investigated and these catalysts show excellent oxidation activity and N2 selectivity for NVOCs oxidation. [26-28] It can be seen that modulating the state of CuO species plays critical role on the catalyzing NVOCs oxidation. However, there is still lack of efficient strategies to further improve the CuO based catalysts for NVOCs oxidation.

CeO<sub>2</sub> modified CuO catalyst could certainly change the performance of catalyst as discussed above, but the effect of CeO<sub>2</sub> and CuO supporting order on the state of CuO is rarely studied. In this work, CeO2 modified CuO/ZSM-5 catalysts were synthesized and the critical role of CeO2 addition order on tuning the state of CuO active sites was revealed. Moreover, there are multi-active sites in the CeO<sub>2</sub> modified CuO/ZSM-5 catalysts including CuO species, Ce<sup>3+</sup> species and the acid sites in ZSM-5 support, which play very important role on the catalytic oxidation activity and N2 selectivity of catalysts for diethylamine (DEA) oxidation (DEA is a typical product from DMF distillation recovery). Different addition order of CeO2 species into the CuO/ZSM-5 catalyst would change the content of active CuO species and Ce<sup>3+</sup> species, resulting in the differentiation of the prepared catalysts. The CuO/CeO2/ZSM-5 catalyst exhibited the widest temperature window ( $\Delta T$ ) for high N<sub>2</sub> selectivity and moderate high catalytic oxidation activity compared with CuO-CeO2/ZSM-5 and CeO2/CuO/ZSM-5 catalysts. We expect this study can offer a useful guideline for further design and fabrication of high performance CuO based catalysts for selective catalytic oxidation of NVOCs.

# 2. Experimental section

#### 2.1. Catalysts synthesis

 $Cu(NO_3)_2 \cdot 3H_2O$  was bought from Sinopharm Chemical Reagent Co. ltd., China. Ce(NO\_3)\_3 \cdot 6H\_2O was obtained from Aladdin Reagent (Shanghai) Co., ltd. ZSM-5 molecular sieve (SiO\_2/Al\_2O\_3 = 18) was purchased from Shandong Dengzhuo Chemical Co., ltd. China. Typical impregnation method was used for preparing CuO/ZSM-5, CuO/CeO\_2 and CeO\_2/ZSM-5 catalysts.

2 g ZSM-5 support was added to a solution containing 1.5 g Cu  $(NO_3)_2 \cdot 3H_2O$ . The mixture was stirred at 30 °C for 1 h before drying at 90 °C. After drying in an oven at 100 °C for 6 h, the solid was calcined at 400 °C for 2 h with a heating rate of 10 °C min<sup>-1</sup>. The obtained catalyst was denoted as CuO/ZSM-5 catalyst (with 20 wt% CuO). CeO<sub>2</sub>/ZSM-5 catalyst with 40 wt% loading of CeO<sub>2</sub> was prepared with the similar procedure to that of CuO/ZSM-5. For the preparation of CuO/CeO<sub>2</sub> (20 wt% CuO), CeO<sub>2</sub> support was obtained by calcining Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O precursor at 400 °C. Other preparation procedures were also similar to the preparation of CuO/ZSM-5 catalyst.

CuO-CeO<sub>2</sub>/ZSM-5 catalyst was prepared by co-impregnation of Cu  $(NO_3)_2$ ·3H<sub>2</sub>O and Ce $(NO_3)_3$ ·6H<sub>2</sub>O on ZSM-5 with similar procedure to that of the CuO/ZSM-5 catalyst. The content of CuO and CeO<sub>2</sub> in the catalyst are 20 and 40 wt%, respectively. And the theoretical content of oxides component (0.5 g CuO, 0.4 g CeO<sub>2</sub> and 1.6 g ZSM-5) are same to the dual oxides catalyst as described below.

 $CuO/CeO_2/ZSM$ -5 catalyst was prepared by sequential impregnation of  $CeO_2$  and CuO on ZSM-5.  $CeO_2$  component was firstly loaded on the ZSM-5 by the typical impregnation method and  $CeO_2/ZSM$ -5 catalyst was obtained, then CuO component was loaded on  $CeO_2/ZSM$ -5 by the same impregnation method.

For the preparation of CeO<sub>2</sub>/CuO/ZSM-5 catalyst, the impregnation order of CeO<sub>2</sub> and CuO on ZSM-5 was adverse to that of CuO/CeO<sub>2</sub>/ZSM-5 catalyst.

# 2.2. Characterization methods

N2 adsorption measurement of catalyst was performed at 77 K on a BK200C system volumetric adsorption analyzer (Beijing Jingwei Gaobo Sci.-Tech. ltd, Beijing, China). Prior to the sorption measurements, the catalyst was degassed at 120 °C for 12 h. The Brunauer-Emmet-Teller (BET) surface area was obtained from the adsorption data at a relative pressure  $(P/P_0)$  in the range of 0.05–0.35. The powder X-ray diffraction (XRD) patterns of catalysts were recorded using a Bruker D8 diffractometer using Cu K $\alpha$  radiation with a scan speed of  $12^{\circ}$  min<sup>-1</sup> from  $2\theta$  of 10 to 90°, operating at 40 kV and 40 mA. Field emission scanning transmission electron microscope (FE-STEM) images and Energy dispersive spectrometer (EDS) analysis were obtained on JEOL-2100F instrument operated at 200 kV. H2-temperature programmed reduction (H2-TPR) experiments were conducted on a lab-made tubular quartz reactor (*i.d.* = 6 mm) equipped with a thermal conductivity detector (TCD). In typical, 35 mg of catalyst was put in the reactor and heated from 30 to 800 °C with a heating ramp of 20 °C min<sup>-1</sup> (in a flow of 5 %  $H_2 + 95 \% N_2$ , 30 mL min<sup>-1</sup>). The signal of gas was recorded using a TCD detector after the H<sub>2</sub>O elimination by solid KOH fixed in a quartz tube. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250Xi instrument with Al  $K_{\alpha}$  source ( $h\nu = 1486.6$  eV). The binding energies (BEs) was calibrated by the carbonaceous C1s line (284.6 eV). Surface acidity of the catalyst was measured by the temperature-programmed desorption of NH3 (NH3-TPD) under a fixed-bed reactor equipped with a mass spectrometer (MS) Ominstar 300. Before measurement, 200 mg of catalyst (60–80 mesh) was heated in He flow (20 mL min<sup>-1</sup>) from 30 to 300 °C (10 °C min<sup>-1</sup>) and kept at 300 °C for 30 min, and then cooled to 100 °C. Afterward, a flow of 10 %  $NH_3 + 90$  % He (30 mL min<sup>-1</sup>) was introduced to the reactor for 10 min at 50 °C for NH<sub>3</sub> adsorption on the catalyst. The gaseous or physically adsorbed NH3 was removed by purging with a He flow (20 mL min<sup>-1</sup>) for 30 min before the MS detector measurement. Finally, the catalyst was heated in the He flow (20 mL  $min^{-1}$ ) from 40 to 700 °C at a rate of 10 °C  $min^{-1}$ , and the desorption of NH3 was detected by MS detector.

### 2.3. Catalytic activity tests

Diethylamine (DEA) oxidation.

The catalytic activity of catalysts for DEA oxidation was performed in a home-made quartz tubular reactor (*i.d.* = 8 mm) with 1 mL catalyst (20–40 mesh, 0.45 g) at atmospheric pressure. A air flow of 5 mL min<sup>-1</sup> was flowed into a bottle with liquid DEA at 0 °C, and then the saturated DEA vapor flow (5 mL min<sup>-1</sup>) was diluted by another air flow of 300 mL min<sup>-1</sup>. The mixture gas consisted of ca. 4200 mg m<sup>-3</sup> DEA was inlet into reactor with a mass space velocity (S.V.) of 20, 000 mL g<sup>-1</sup>h<sup>-1</sup>. DEA vapor concentration was determined by an online gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and an SH-Stabliwax-DB capillary column (30 m × 0.32 mm). DEA conversion can be calculated by the following equation:

 $Conversion = ([C]_{in} - [C]_{out})/[C]_{in} \times 100 \%.$ 

where [C]in and [C]out are DEA concentrations in the inlet and outlet gas, respectively.

 $NO_x$  and CO were analyzed by flue gas analyzer (ecom-EN3, ECOM, Germany), and no  $NH_3$  was detected. The selectivity of  $N_2$  was calculated by the following equation:

$$Selectivity(N_2) = (1 - \frac{actual NOx yield}{theoretical NOx yield}) \times 100\%$$
(1)

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Simultaneously, the selectivity of CO is also calculated by the ratio of actual CO concentration and theoretical CO concentration.

Diethyl ether (DE) oxidation reaction

The process of DE oxidation activity evaluation is same to that of DEA above. The gaseous DE concentration is 8800 mg m<sup>-3</sup> DE. Other procedures were same to DEA oxidation reaction.

#### 3. Result and discussion

# 3.1. Catalyst structure and surface active oxides analyses

Phase composition and active oxides properties of all as-prepared CuO based catalysts were characterized (Fig. 1 and Table 1). For the XRD pattern of the bare ZSM-5 support (Fig. 1a), the characteristic diffraction peaks are in line with the typical MFI structure (JCPDS No. 44–0003). [17,20] Compared to ZSM-5 support, two new characteristic diffraction peaks appear at 35.4 and 38.7° for the CuO/ZSM-5 catalyst which are attributed to the (002) and (111) facets of crystalline phase CuO (JCPDS No. 48–1548). [20–21] For the XRD pattern of CuO/CeO<sub>2</sub> catalyst, the characteristic diffraction peaks at 28.6, 33.1, 47.6 and 56.5° are ascribed to (111), (200), (220) and (311) facets of cubic fluorite structure CeO<sub>2</sub> (JCPDS No. 81-0792), respectively; [29] the characteristic diffraction peaks of CuO species were also observed. For the dual oxides catalysts (CuO-CeO2/ZSM-5, CuO/CeO2/ZSM-5 and CeO2/CuO/ ZSM-5) catalysts, the characteristic diffraction peaks of both CuO and CeO<sub>2</sub> can be clearly found in addition to the diffraction peaks of ZSM-5 support. Additionally, the crystallite size of the CuO and CeO<sub>2</sub> particles were calculated by Scherrer equation according to XRD data (Table 1). [21,30] The CuO/CeO<sub>2</sub> catalyst shows the largest size (ca. 28.7 nm) of CuO particles because of low surface area of CeO<sub>2</sub> support. On contrast, the CuO/ZSM-5 catalyst has smallest CuO particles of 20.1 nm due to the high surface area of ZSM-5 support. For the dual oxides catalysts (CuO-  $CeO_2/ZSM-5$ ,  $CuO/CeO_2/ZSM-5$  and  $CeO_2/CuO/ZSM-5$ ) prepared with different impregnation sequence, the  $CeO_2/CuO/ZSM-5$  catalyst has the relatively smaller CuO particles compared to other two catalysts. Particle size of  $CeO_2$  species supported on ZSM-5 slightly decreases in comparison to the pure  $CeO_2$  support.

To understand the distribution of (Table 2) CeO<sub>2</sub> and CuO on the catalyst surface, surface atomic ratio Cu/Ce and surface chemical valance of oxides (CuO, CeO<sub>2</sub>) are also analyzed (Fig. 1b-c, Table 1). Surface atomic ratio Cu/Ce of the CuO/CeO<sub>2</sub> catalyst is slightly higher than theoretical value due to partial CeO2 surface covered by CuO. For the dual oxides catalysts (CuO-CeO2/ZSM-5, CuO/CeO2/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5), only the CuO-CeO<sub>2</sub>/ZSM-5 catalyst shows a surface atomic ratio Cu/Ce comparable to the theoretical value. Both the CuO/ CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalysts show lower surface atomic ratio Cu/Ce than the theoretical value. Such findings indicate that CeO<sub>2</sub> specie is easier to be highly dispersed on the ZSM-5 surface compared to CuO specie, and the co-impreginated CeO2 species increase the CuO dispersion on the catalyst surface. Fig. 2 shows the STEM and element mapping images of the CuO/CeO<sub>2</sub>/ZSM-5 catalyst, which also confirms that Ce element is uniformly distributed whereas majority of Cu element is aggregated generating particle on catalyst surface.

XPS technique was used to study the surface valance of CuO and CeO<sub>2</sub> (Fig. 1b-c, Table 1). In the Cu 2*p* spectra of these catalysts, the components with binding energies at 931 ~ 938 and 951 ~ 958 eV are assigned to Cu 2*p*<sub>3/2</sub> and Cu 2*p*<sub>1/2</sub>, respectively. [30–32] The component of Cu 2*p*<sub>3/2</sub> can be deconvoluted into signal at 932.5, 933.5 and 935.8 eV, which corresponds to Cu<sup>+</sup> specie, large size bulk CuO specie ( $\alpha$ -Cu<sup>2+</sup>) and highly dispersed Cu<sup>2+</sup> specie ( $\beta$ -Cu<sup>2+</sup>), respectively. [20,26] The peak with binding energy at 941 ~ 945 eV is assigned to the satellite peak of Cu 2*p*<sub>3/2</sub>. For the deconvoluted Ce 3*d* spectra, the peaks denoted to "v" correspond to component of Ce 3*d*<sub>3/2</sub> spectra. The



Fig. 1. A) XRD patterns, b) H<sub>2</sub>-TPR profiles, XPS spectra of c) Cu 2*p* and d) Ce 3*d* of CuO/CeO<sub>2</sub>, CuO/ZSM-5, CuO-CeO<sub>2</sub>/ZSM-5, CuO/CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalyst, e) XRD pattern of spent catalysts after NH<sub>3</sub>-TPD test and f) colour change of CuO/CeO<sub>2</sub>/ZSM-5 catalyst after NH<sub>3</sub>-TPD.

#### Table 1

The surface area, oxide particles size, surface elements (Cu and Ce) chemical states of catalysts.

Catalyst	BET surface area <sup>a</sup> /m <sup>2</sup> ·g <sup>-1</sup>	CuO content (w.t.%)	CeO <sub>2</sub> content (w.t.%)	CuO size <sup>b</sup> /nm	CeO <sub>2</sub> size <sup>b</sup> /nm	Theoretical atomic ratio Cu/Ce	Surface atomic ratio Cu/Ce <sup>c</sup>	Cu <sup>+</sup> /Cu (%) <sup>c</sup>	α-Cu <sup>2+</sup> / Cu (%) <sup>c</sup>	β-Cu <sup>2+</sup> / Cu (%) <sup>c</sup>	Ce <sup>3+</sup> / (Ce <sup>3+</sup> +Ce <sup>4+</sup> ) (%) <sup>c</sup>
CuO/CeO <sub>2</sub>	83	20	80	28.7	8.6	0.53	0.67	15	55	30	12
CuO/ZSM-5	161	20	-	20.1	-	-	-	2	57	41	-
CeO2/ZSM-	229	-	20	-	6.1	-	-	-	-	-	17
5											
CuO-CeO <sub>2</sub> /	103	20	16	23.6	4.7	2.70	2.73	7	61	32	12
ZSM-5											
CeO2/CuO/	112	20	16	22.4	5.8	2.70	1.08	10	52	38	13
ZSM-5											
CuO/CeO <sub>2</sub> /	111	20	16	25.2	5.1	2.70	1.27	4	57	39	15
ZSM-5											

<sup>a</sup> BET surface area was measured by N<sub>2</sub> adsorption at 77 K;

<sup>b</sup> crystallite size was calculated by Scherrer equation;

<sup>c</sup> Determined by XPS spectra.

### Table 2

The T<sub>99</sub>, selectivity of N<sub>2</sub> and CO at T<sub>99</sub> and temperature window  $\Delta T$  for high N<sub>2</sub> selectivity of DEA oxidation over CuO-based catalysts.

Catalyst	T99 <sup>ª</sup> ∕ °C	$S_{N2}^{b}$ /% at T <sub>99</sub>	S <sub>CO</sub> <sup>c</sup> / at T <sub>99</sub>	T <sub>N2</sub> <sup>d</sup> / °C	$\triangle T^{e} = T_{N2} - T_{99}$ / $^{o}C$
CuO/CeO <sub>2</sub>	200	100	0	220	20
CuO/SiO <sub>2</sub>	340	96.3	0	-	-
CuO/Al <sub>2</sub> O <sub>3</sub>	320	89.3	0	-	-
CuO/ZSM-5	240	99.5	0.2	340	100
CuO-CeO2/ZSM-5	220	100	0	340	120
CeO2/CuO/ZSM-5	220	100	0	360	140
CuO/CeO2/ZSM-5	230	100	0	380	150

<sup>a</sup>  $T_{99}$ : the temperature for DEA conversion of 99%.

<sup>b</sup>  $S_{N2}$ : the N<sub>2</sub> selectivity.

<sup>c</sup>  $S_{\rm CO}$ : the CO selectivity.

<sup>d</sup>  $T_{N2}$ : the highest temperature for N<sub>2</sub> selectivity of 99%.

<sup>e</sup>  $\Delta T$ : the temperature window for high N<sub>2</sub> selectivity (>99 %).

peaks of v' (884.4 eV) and u' (903.3 eV) could be assigned to the Ce  $3d_{5/2}$  $^{2}_{2}$  and  $3d_{3/2}$  spectra of  $Ce^{3+}$  species, while other peaks are attributed to the Ce  $3d_{5/2}$  (v: 882.5 eV; v'': 885.6 eV; v''': 889.4 eV) and  $3d_{3/2}$  (u: 901.3 eV; u'': 907.8 eV; u''': 917.0 eV) spectra of the Ce<sup>4+</sup> species, suggesting the multiple oxidation states of Ce species in the catalysts. [33–37] There are dominant  $Ce^{4+}$  species in the  $CeO_2$  lattice according to the ratio of  $Ce^{3+}/Ce^{4+}$ . The appearance of  $Ce^{3+}$  species represents the existence of oxygen vacancies on the catalyst surface. It can be seen that  $CeO_2$  addition order affects the ratio of  $Ce^{3+}$  species on the catalyst surface, the CuO/CeO<sub>2</sub>/ZSM-5 catalyst has the highest ratio of Ce<sup>3+</sup> species in comparison with the CuO-CeO2/ZSM-5 and CuO/CeO2/ZSM-5 catalysts. Additionally, compared to the CuO/ZSM-5 catalyst, the CuO/ CeO<sub>2</sub> catalyst has more surface Cu<sup>+</sup> species. Also, the surface Cu<sup>+</sup> species increased in the dual oxides catalysts (CuO-CeO2/ZSM-5, CuO/ CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5) in comparison with that of CuO/ ZSM-5 catalyst, suggesting CeO<sub>2</sub> species could significantly enhance the reducibility of CuO species. The CeO2/CuO/ZSM-5 catalyst shows the most surface Cu<sup>+</sup> species in these dual oxides catalysts.

H<sub>2</sub>-TPR tests were performed to investigate reducibility of active



Fig. 2. STEM image and element mapping images of CuO/CeO<sub>2</sub>/ZSM-5 catalyst.

oxides in these CuO based catalysts (Fig. 1d). No remarkable reduction peak appears in the CeO2/ZSM-5 catalyst and previous works also reported that  $CeO_2$  species are reduced at high temperature > 350 °C, [31] suggesting the reduction peak in these CuO based catalysts are mainly attributed to the reduction of CuO species. For the CuO/CeO2 catalyst, there are three reduction peaks in the temperature range of 160–280 °C. The peak centered at 186 °C is ascribed to the reduction of Cu<sup>+</sup> specie, a highly active site; [35] the peak centered at 201 °C corresponds to the reduction of surface finely dispersed CuO ( $\alpha$ -Cu<sup>2+</sup>, [38–40,42,43] the reduction peak at higher temperature of 240 °C is attributed to the large size bulk CuO specie ( $\beta$ -Cu<sup>2+</sup>). [39–41] Two reduction peaks are observed for the CuO/ZSM-5 catalyst, the peak centered at 223 °C is assigned to the reduction of highly dispersed CuO cluster on ZSM-5 surface ( $\alpha$ -Cu<sup>2+</sup>), and the peak centered at 269 °C is attributed to the reduction of large size bulk CuO ( $\beta$ -Cu<sup>2+</sup>). For the dual oxides catalysts (CuO-CeO<sub>2</sub>/ZSM-5, CuO/CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5), the CuO specie reduction peaks remarkably shift to lower temperature, suggesting CeO<sub>2</sub> promotes the reduction of CuO. The high reducibility of CuO species in the ZSM-5 supported CuO catalysts can also be evidenced by the XRD pattern of the spent CuO/CeO<sub>2</sub>, CuO/ZSM-5, CuO/CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalysts after NH<sub>3</sub>-TPD test (Fig. 1e-f). It can be found that CuO species are remained for the CuO/CeO<sub>2</sub> catalyst after NH3-TPD test, whereas CuO species are completely transformed to Cu2O species for the CuO/CeO2/ZSM-5 and CeO2/CuO/ZSM-5 catalysts. For the CuO/ZSM-5 catalyst, most of CuO species have been even transformed to metallic Cu species in addition to generating minority of Cu<sub>2</sub>O species after NH<sub>3</sub>-TPD test. This result suggests ZSM-5 support plays critical role on the reduction of CuO by NH<sub>3</sub>, whereas CeO<sub>2</sub> species stabilize Cu<sub>2</sub>O species and prevent it to further be reduced to metallic Cu species.

# 4. Surface acid sites analyses

Surface acidity of catalyst was studied by NH3-TPD test, and the desorbed substances were detected by MS detector (Fig. 3 and Fig. S1-3). It can be seen that only the CuO/CeO2 catalyst shows very weak NH3 desorption peaks at 200 °C, suggesting the deficient acid sites on the CuO/CeO<sub>2</sub> catalyst. Whereas, ZSM-5 support shows very strong NH<sub>3</sub> desorption peaks (Fig. S1), thus, it is reasonable to infer that those  $NH_3$ desorption peaks in CuO/ZSM-5 and CeO2 modified CuO/ZSM-5 catalysts are attributed to the acid sites in ZSM-5·NH<sub>3</sub> desorption from weak acid sites, moderate strong acid sites and strong sites appear at temperature of < 200, 200–400 and > 400 °C, respectively. [44–45] Interestingly, in addition to NH<sub>3</sub> signal, there are also N<sub>2</sub>, NO and H<sub>2</sub>O signals appearing in the NH<sub>3</sub>-TPD profiles of the CuO/ZSM-5 and CeO<sub>2</sub> modified CuO/ZSM-5 catalysts. Such finding can be attributed to the oxidation-reduction reaction of NH3 on these catalysts surface. Moreover, the CuO/CeO<sub>2</sub>/ZSM-5 catalyst shows the strongest N<sub>2</sub> signal and no NO signal, implying the high selectivity to N<sub>2</sub> during the oxidation-reduction reaction. However, there is very strong NO signal appearing at 100-300 °C for the CuO/ZSM-5, CeO<sub>2</sub>/CuO/ZSM-5 and CuO-CeO<sub>2</sub>/ZSM-5 catalysts, which is ascribed to the over-oxidized NH<sub>3</sub> process-NH<sub>3</sub>-TPD profile of ZSM-5 support shows only NH<sub>3</sub> signal without any N2, NO and H2O signals, indicating the absence of oxidation-reduction reaction of NH3 on the ZSM-5 surface. For comparison, NH3-TPD tests were also conducted for the CuO/SiO2 and CuO/Al2O3 catalysts, and no signals of N2 and NO were observed (Fig. S2-3). The above results suggest both CuO and the acid sites of ZSM-5 enable the oxidation-reduction of NH<sub>3</sub>, and CeO<sub>2</sub> enhances the N<sub>2</sub> selectivity as observed on the CuO/CeO<sub>2</sub>/ZSM-5 catalyst. Fig. 3f shows the pyridine chemisorbed FT-IR spectra to further investigate the surface acid sites on these CuO based catalysts. The vibration peaks at 1450 and 1545 cm<sup>-1</sup> are ascribed to the pyridine absorbed on Lewis and Bronsted acid sites,



Fig. 3. a-e) NH<sub>3</sub>-TPD profiles and f) Pyridine chemisorbed FT-IR spectra of CuO/CeO<sub>2</sub>, CuO/ZSM-5, CuO-CeO<sub>2</sub>/ZSM-5, CuO/CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalysts.

respectively. [46–47] It can be seen that the CuO/CeO<sub>2</sub> catalyst shows weak vibration peak at 1450 cm<sup>-1</sup> and no vibration peak at 1545 cm<sup>-1</sup>, further confirming its deficient acid sites as discussed in NH<sub>3</sub>-TPD profile. For the ZSM-5 supported catalysts, the vibration peaks at 1450 and 1545 cm<sup>-1</sup> are very strong due to abundant acid sites in the ZSM-5.

# 5. Catalytic performance for DEA oxidation

The complete oxidation of DEA involving both hydrocarbon species oxidation and N element selective transformation into N<sub>2</sub>, although the by-product of NO<sub>x</sub> is undesired but could react with DEA to generate N<sub>2</sub> which is regarded as SCR reaction as described in following expressions<sup>21</sup>, [26]:

$$(CH_3CH_2)_2NH + O_2 \rightarrow CO_2 + H_2O + NO_x \tag{1}$$

$$(CH_3CH_2)_2NH + NO_x \rightarrow CO_2 + H_2O + N_2 \tag{2}$$

Thus, balance of catalytic oxidation activity and SCR activity (NO<sub>x</sub> with DEA) is the key to control the N<sub>2</sub> selectivity. Fig. 4 and Fig S4 shows the catalytic performance for DEA oxidation over the CuO based catalysts. For the DEA catalytic oxidation, the CuO/CeO<sub>2</sub> catalyst has the

highest oxidation activity with T<sub>99</sub> at 200 °C, and the CuO/ZSM-5 catalyst exhibits the moderate high oxidation activity ( $T_{99} = 240 \ ^{\circ}C$ ), whereas the CuO/Al2O3 and CuO/SiO2 catalysts show the inferior catalytic oxidation with higher T<sub>99</sub> temperature. The CuO-CeO<sub>2</sub>/ZSM-5 catalyst presents the enhanced catalytic oxidation in comparison with the CuO/ZSM-5 catalyst. Such findings suggest that CeO2 could improve the oxidation activity of CuO species. The catalysts with lower T<sub>99</sub> also show the lower CO selectivity (Fig. 3c), further confirming the higher catalytic oxidation activity. However, the order of N2 selectivity of these CuO based catalysts is very different from that of catalytic oxidation activity, such as the CuO/CeO2 catalyst shows the lowest N2 selectivity. To clearly understand the changes of N2 selectivity in these catalysts, temperature window ( $\Delta T$ ) for high N<sub>2</sub> selectivity has been analyzed. $\Delta T$  represents the temperature range after  $T_{99}$  in which N<sub>2</sub> selectivity is higher than 99 %. It can be seen that the CuO/CeO2 catalyst shows very narrow temperature window ( $\Delta T$ ) of 20 °C, and there is no temperature range for the CuO/Al\_2O\_3 and CuO/SiO\_2 catalysts with  $N_{\rm 2}$ selectivity > 99 % after T<sub>99</sub>. The CuO/ZSM-5 catalyst exhibits the comparable temperature window ( $\Delta T$ ) to the CuO-CeO<sub>2</sub>/ZSM-5 catalyst, but the CuO-CeO<sub>2</sub>/ZSM-5 catalyst shows better performance to eliminate the by-product of CO. The effect of mass ratio of CeO<sub>2</sub>/ZSM-5



Fig. 4. The catalytic performance of CuO-based catalysts for the DEA oxidation.

on catalytic performance has also been studied in Fig. S4, it can be seen that the catalyst with mass ratio CeO<sub>2</sub>/ZSM-5 of 1/4 exhibits the superior oxidation activity and N<sub>2</sub> selectivity compared to others. Additionally, the addition sequence of CeO<sub>2</sub> to CuO/ZSM-5 catalyst also significantly affects the catalytic performance. Among the CuO-CeO<sub>2</sub>/ZSM-5, CuO/CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalysts, the CeO<sub>2</sub>/CuO/ZSM-5 catalyst obviously shows the lowest T<sub>99</sub> for DEA oxidation, but the CuO/CeO<sub>2</sub>/ZSM-5 catalyst shows the widest temperature window ( $\Delta T$ ) of 150 °C with high N<sub>2</sub> selectivity for DEA oxidation (Fig. 3d-e). In terms of controlling VOCs, CO and NO<sub>x</sub> pollution, the CuO/CeO<sub>2</sub>/ZSM-5 catalyst should be more suitable for catalytic oxidation DEA in application due to its widest temperature window (Fig. 5).

### 6. Discussion

CeO<sub>2</sub> significantly affected the state of CuO species, Cu<sup>+</sup> species and the finely dispersed CuO ( $\alpha$ -Cu<sup>2+</sup>) species are critical active sites for oxidation reaction. The content of these highly active Cu species in catalysts is in order of CuO/CeO<sub>2</sub> (70 %) > CuO-CeO<sub>2</sub>/ZSM-5 (68 %) >CeO<sub>2</sub>/CuO/ZSM-5 (62 %) > CuO/CeO<sub>2</sub>/ZSM-5 (61 %) > CuO/ZSM-5 (59 %). Thus, the CuO/CeO<sub>2</sub> catalyst shows the highest oxidation activity with T<sub>99</sub> of 200 °C, whereas the CuO/ZSM-5 catalyst exhibits the lowest oxidation activity. After introduction of CeO2, ZSM-5 supported dual oxides (CuO-CeO2/ZSM-5, CuO/CeO2/ZSM-5 and CeO2/CuO/ZSM-5) catalysts display the increased oxidation compared with the CuO/ ZSM-5 catalyst, which is ascribed to the increased content of Cu<sup>+</sup> and  $\alpha$ -Cu<sup>2+</sup> species. Additionally, the Ce<sup>3+</sup> specie would enhance the oxidation activity of Cu species, thus CeO2/CuO/ZSM-5 (62 %) has lower content of active Cu species in comparison with CuO-CeO2/ZSM-5 (68 %), they show the comparable oxidation activity due to  $CeO_2/CuO/$ ZSM-5 containing slightly more  $Ce^{3+}$  specie (13 %). Also, the CuO/  $CeO_2/ZSM$ -5 catalyst shows the comparable content of  $Cu^+$  and the finely dispersed CuO ( $\alpha$ -Cu<sup>2+</sup>) to the CuO/ZSM-5 catalyst (61 %vs 59 %), the CuO/CeO2/ZSM-5 catalyst presents higher oxidation activity (T99 of 230 °C) because the promotional role of  $Ce^{3+}$  on Cu active sites.

To further confirm the changes of catalytic oxidation activity for the CeO<sub>2</sub> modified CuO/ZSM-5 catalyst, the model oxidation reaction of diethyl ether (DE) was conducted over the CuO/ZSM-5, CuO-CeO<sub>2</sub>/ZSM-5, CeO<sub>2</sub>/CuO/ZSM-5 and CuO/CeO<sub>2</sub>/ZSM-5 catalysts because of the similar structure of DE to DEA. It can be seen that all these ZSM-5 supported dual oxides catalysts show the increased catalytic oxidation activity for DE oxidation, which is consistent with the oxidation activity order for DEA oxidation. The CuO/CeO<sub>2</sub>/ZSM-5 catalyst shows the moderate high catalytic oxidation for DE oxidation.

It is necessary to combine the NH<sub>3</sub>-TPD profiles to further discuss the N<sub>2</sub> selectivity changes of DEA oxidation over these CuO based catalysts.

According to the profiles of ZSM-5, CuO/CeO<sub>2</sub>, CuO/SiO<sub>2</sub> and CuO/ Al<sub>2</sub>O<sub>3</sub>, it can be inferred that active CuO species and acid sites on ZSM-5 are important for N<sub>2</sub> formation in NH<sub>3</sub> oxidation during NH<sub>3</sub>-TPD. N<sub>2</sub> signal appearing in the NH3-TPD profiles of the CuO/ZSM-5 and CeO2 modified catalysts indicates that the oxidation-reduction reaction of NH<sub>3</sub> takes place on the catalysts surface. It should be mentioned that NO signal is absent in the NH<sub>3</sub>-TPD profile of CuO/CeO<sub>2</sub>/ZSM-5 catalyst in the experiment temperature range. Such finding suggest the highest N<sub>2</sub> selectivity of CuO/CeO2/ZSM-5 for NH3 oxidation. Compare with CuO-CeO<sub>2</sub>/ZSM-5 and CeO<sub>2</sub>/CuO/ZSM-5 catalysts, most Ce<sup>3+</sup> species in the CuO/CeO<sub>2</sub>/ZSM-5 catalyst may account for the highest N<sub>2</sub> selectivity, because the Ce<sup>3+</sup> species are critical active sites for SCR reaction. [26–27] Therefore, it can also explain that the  $CuO/CeO_2/ZSM-5$  catalyst exhibits the widest temperature window for N2 selectivity in the DEA oxidation due to the critical role of  $Ce^{3+}$  species in addition active CuO and acid sites on ZSM-5.

# 7. Water resistance

Water resistance is also very important performance indicators of an potential industrial catalyst. Thus, the representative CuO/CeO<sub>2</sub>/ZSM-5 catalyst with superior N<sub>2</sub> selectivity was employed for catalyzing DEA oxidation under wet condition (5 % H<sub>2</sub>O) as shown in Fig. 6. It can be seen that water steam has no influence on the complete oxidation temperature of DEA over the CuO/CeO<sub>2</sub>/ZSM-5 catalyst (Fig. 6a), and its N<sub>2</sub> selectivity slightly increases in presence of water steam; however, the production of CO also increases which is unexpected. The CeO<sub>2</sub>/CuO/ZSM-5 catalyst shows very robust stability and N<sub>2</sub> selectivity for catalyzing DEA oxidation at 260 °C under wet condition (5 % H<sub>2</sub>O), suggesting the catalytic active sites in this catalyst are water tolerant.

# 8. Conclusion

In summary, CeO<sub>2</sub> modified CuO/ZSM-5 catalysts (CuO-CeO<sub>2</sub>/ZSM-5, CeO<sub>2</sub>/CuO/ZSM-5 and CuO/CeO<sub>2</sub>/ZSM-5) were prepared for DEA catalytic oxidation. The sequence of CeO<sub>2</sub> addition affects the geometrical and electronic states of CuO species on the ZSM-5 support, thus, the catalytic oxidation activity of CuO/ZSM-5 catalyst has been modulated. The CeO<sub>2</sub>/CuO/ZSM-5 and CuO-CeO<sub>2</sub>/ZSM-5 catalysts have more CuO species being easily reduced (such as Cu<sup>+</sup> species and finely dispersed CuO clusters) which is responsible for their lower T<sub>99</sub> in DEA oxidation in comparison with CuO/CeO<sub>2</sub>/ZSM-5 catalyst. However, the CuO/CeO<sub>2</sub>/ZSM-5 catalyst shows the widest temperature window of 150 °C with high N<sub>2</sub> selectivity for catalyzing DEA oxidation. It is revealed that the Ce<sup>3+</sup> species, in addition to CuO species and the acid sites on the ZSM-5, also play critical role on tuning the N<sub>2</sub> selectivity.



Fig. 5. The catalytic performance of CuO-based catalysts for the DE oxidation.



Fig. 6. The catalytic performance of CuO/CeO2/ZSM-5 catalyst for the DE oxidation.

# CRediT authorship contribution statement

Lin-Cong He: Conceptualization, Data curation, Formal analysis, Investigation, Writing – original draft. Hua-Hui Xu: Conceptualization, Data curation, Formal analysis, Investigation. Xing-Yue Leng: Conceptualization, Data curation, Formal analysis, Visualization. Ling-Yun Jin: Conceptualization, Investigation, Resources, Data curation, Funding acquisition. Ai-Ping Jia: Software, Visualization, Funding acquisition. Meng-Fei Luo: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Project administration, Supervision, Writing – review & editing. Jian Chen: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Software, Methodology, Supervision, Writing – review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

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